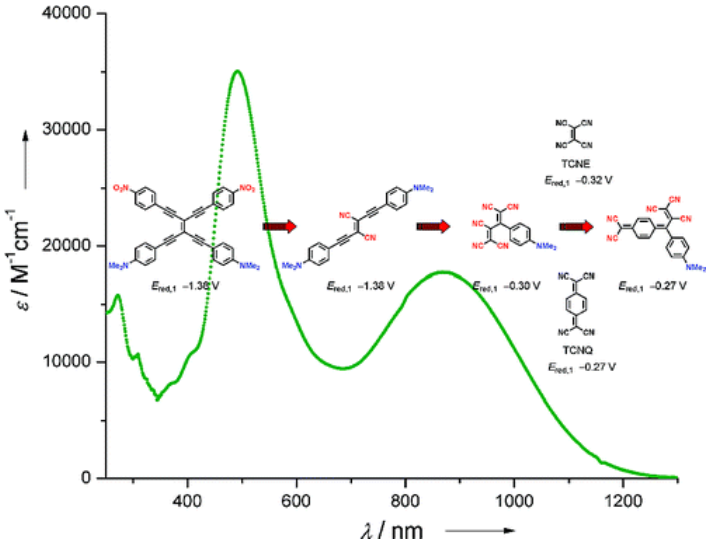
- Acetylene-Derived Strong Organic Acceptors for Planar and Nonplanar Push−Pull Chromophores
  Kivala, M.; Diederich, F. *Acc. Chem. Res.* **2009**, *42*, 235–248.
  Abstract:



Though investigated for decades, interest in push−pull chromophores (D−π−A), strong electron donors (D) connected by π-conjugating spacers to strong electron acceptors (A), continues to grow. Such chromophores are of substantial interest for optoelectronic devices such as waveguides. Also, strong donors and acceptors form bimolecular charge-transfer (CT) complexes and salts, some of which exhibit electrical conductivity and magnetic behavior. Furthermore, strong organic acceptors are increasingly explored as dopants in the fabrication of organic light-emitting diodes (OLEDs) and solar cells. This Account describes systematic efforts pursued over the past decade in our laboratory to generate new families of organic electron acceptors (A) and conjugate them via π-spacers to electron donors (D) under formation of push−pull systems with intense intramolecular CT interactions and high third-order optical nonlinearities.

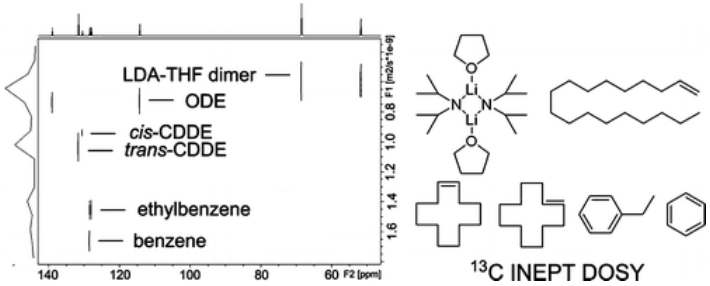
First, we describe donor−acceptor-substituted tetraethynylethenes (TEEs). In these chromophores, the peripherally attached *p*-nitrophenyl acceptors and *N*,*N*-dimethylanilino donors behave as nearly independent redox centers. Acetylenic scaffolding using TEE building blocks produces large all-carbon sheets, such as perethynylated dehydroannulenes, expanded radialenes, and radiaannulenes with potent electron-acceptor properties. Arylated TEEs act as molecular switches allowing two-way photochemical interconversion that is not perturbed by thermal isomerization pathways.

Upon sequential substitution of the acetylene moieties in TEEs, we formed another family of potent acceptors, the cyanoethynylethenes (CEEs). Donor-substituted CEEs are planar CT chromophores with very high third-order optical nonlinearities. Their high environmental stability allows for the formation of thin films by vapor-phase deposition. Through careful analysis of the physicochemical properties of CEEs, we established useful guidelines for evaluating and tuning the optical gap in strong push−pull chromophores: increasing the length of the π-spacer in D−π−A systems reduces ground-state D−A conjugation and lowers the HOMO−LUMO gap.

By taking advantage of “click-chemistry”-type [2 + 2] cycloadditions of tetracyanoethene (TCNE) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) with appropriately activated alkynes, followed by retro-electrocyclization, the formation of donor-substituted 1,1,4,4-tetracyanobuta-1,3-dienes (TCBDs), 1,1,2,4,4-pentacyanobuta-1,3-dienes (PCBDs), and novel TCNQ adducts is possible. Some of these stable, nonplanar CT chromophores form high optical quality amorphous thin films by vapor-phase

deposition. Despite donor substitution, the new acceptors (TCBDs, PCBDs, and the TCNQ adducts) rival TCNE and TCNQ in their ease for reversible electron uptake. High-yielding cycloaddition/retro-electrocyclization cascades provide access to multivalent, dendritic chromophores acting as "molecular batteries" with a remarkable capacity for multiple electron uptake in a narrow potential range. Finally, we used a one-pot protocol for electronically controlled consecutive TCNE and tetrathiafulvalene (TTF) additions to end-capped polyynes to form [AB]-type oligomers with a dendralene-type backbone.

- Characterization of Reactive Intermediates by Multinuclear Diffusion-Ordered NMR Spectroscopy (DOSY)
  Li, D.; Keresztes, I.; Hopson, R.; Williard, P. G. *Acc. Chem. Res.* **2009**, *42*, 270–280.
  Abstract:

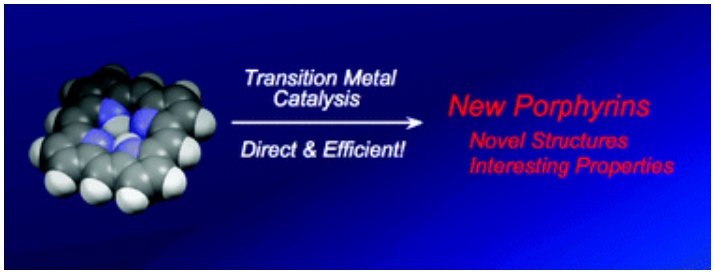


Nuclear magnetic resonance (NMR) is the most powerful and widely utilized technique for determining molecular structure. Although traditional NMR data analysis involves the correlation of chemical shift, coupling constant, and NOE interactions to specific structural features, a largely overlooked method introduced more than 40 years ago, pulsed gradient spin−echo (PGSE), measures diffusion coefficients of molecules in solution, thus providing their relative particle sizes. In the early 1990s, the PGSE sequence was incorporated into a two-dimensional experiment, dubbed diffusion-ordered NMR spectroscopy (DOSY), in which one dimension represents chemical shift data while the second dimension resolves species by their diffusion properties. This combination provides a powerful tool for identifying individual species in a multicomponent solution, earning the nickname "chromatography by NMR". In this Account, we describe our efforts to utilize DOSY techniques to characterize organometallic reactive intermediates in solution in order to correlate structural data to solid-state crystal structures determined by X-ray diffraction and to discover the role of aggregate formation and solvation states in reaction mechanisms.

In 2000, we reported our initial efforts to employ DOSY techniques in the characterization of reactive intermediates such as organolithium aggregates. Since then, we have explored DOSY experiments with various nuclei beyond ^{1}H, including ^{6}Li, ^{7}Li, ^{11}B, ^{13}C, and ^{29}Si. Additionally, we proposed a diffusion coefficient−formula weight relationship to determine formula weight, aggregation number, and solvation state of reactive intermediates. We also introduced an internal reference system to correlate the diffusion properties of unknown reactive intermediates with known inert molecular standards, such as aromatic compounds, terminal olefins, cycloolefins, and tetraalkylsilanes. Furthermore, we utilized DOSY to interpret the role of aggregation number and solvation state of organometallic intermediates in the reactivity, kinetics, and mechanism of organic reactions. By utilizing multinuclear DOSY methodologies at various temperatures, we also correlated solid-state X-ray structures with those in solution and discovered new reactive complexes, including a monomeric boron enolate, a product-inhibition aggregate, and a series of intermediates in the vinyl lithiation of allyl amines. As highlighted by our efforts, DOSY techniques provide practical and feasible NMR

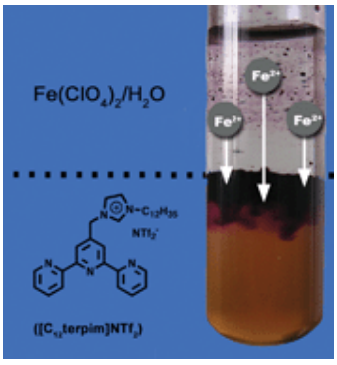
procedures and hold the promise of even more powerful insights when extended to three-dimensional experiments.

- Marriage of porphyrin chemistry with metal-catalysed reactions
  Shinokubo, H.; Osuka, A. *Chem. Commun.* **2009**, 1011 – 1021.
  Abstract :



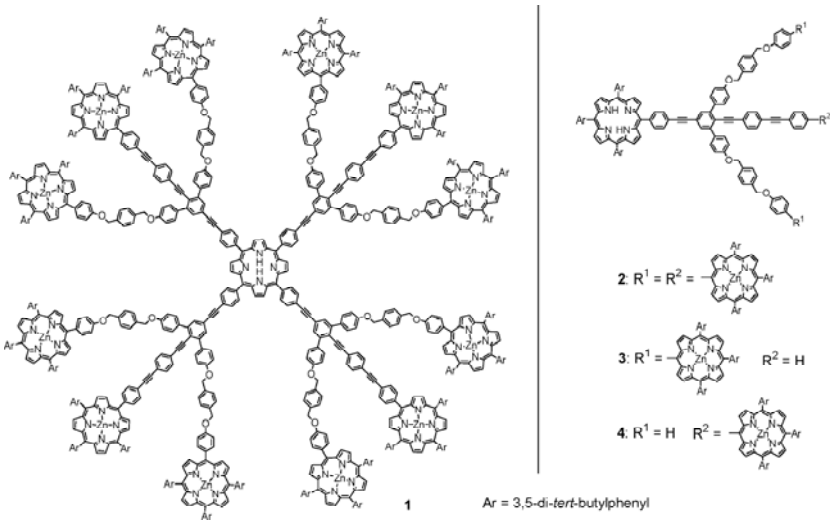
The development of porphyrin synthesis by means of transition metal-catalyzed reactions is explored in this feature article. Porphyrins have been receiving much attention in a wide area of chemistry as functional dyes, non-linear optical materials, ligands for a variety of metals, structural motifs in supramolecules, and so forth. However, they have been merely recognized as a reaction substrate in transition metal-catalyzed transformations. Recently, application of such new methodologies to porphyrin synthesis has proven to be very powerful to create new types of porphyrinic compounds, which have their own intriguing structures and properties. New transformations on porphyrins *via* transition metal catalysis offer us prospects of new designs of architectures, thus facilitating further development of this important class of functional molecules.

- Terpyridine-functionalized imidazolium ionic liquids.
  Olivier, J. H.; Camerel, F.; Selb, J.; Retailleau, P.; Ziessel , R. *Chem. Commun.* **2009**, 1133 – 1135.
  Abstract :



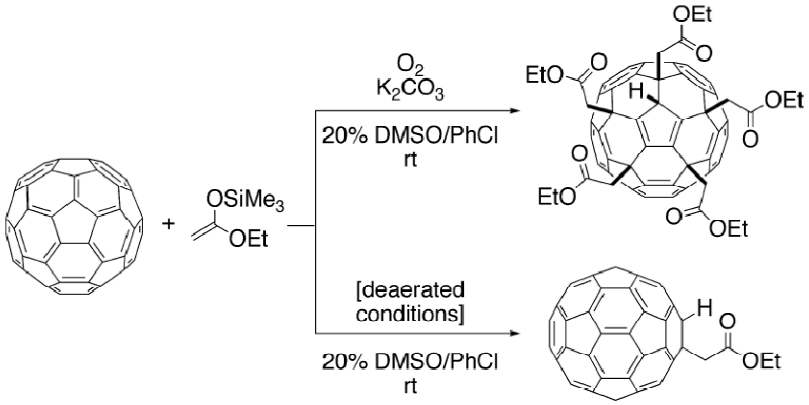
This paper reports the synthesis and the physical characterization of a new family of chelating ionic liquids carrying a terpyridine fragment suitable for metal extraction.

- A Light-Harvesting Array Composed of Porphyrins and Rigid Backbones
  Kozaki M.; Uetomo A.; Suzuki S.; Okada K. *Org. Lett*. **2008**, *10*, 4477-4480
  Abstract :



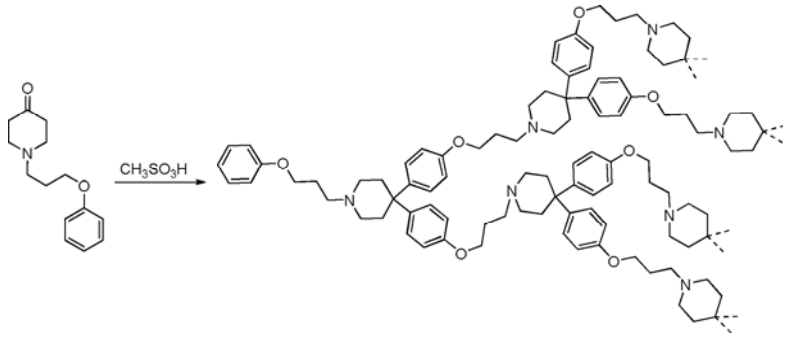
A light-harvesting array containing rigid backbones, peripherally positioned Zn-porphyrin terminals, and a free-base (Fb) porphyrin core was prepared by a convergent method where the Sonogashira coupling reaction was used in the key steps. Effective intramolecular singlet-energy transfer from the peripheral Zn-porphyrin units to the Fb porphyrin core was observed. The efficiency of the energy transfer was compared with those of reference compounds.

- Mono- and Penta-Addition of Enol Silyl Ethers to [60]Fullerene
  Nakamura E.; Mouri S.; Nakamura Y.; Harano K.; Isobe H. *Org. Lett.*, **2008**, *10*, 4923-4926.
  <u>Abstract :</u>



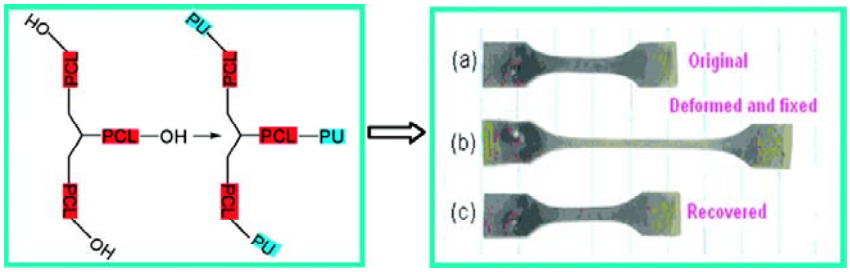
The reaction of 1-alkoxy-1-siloxyethene with [60]fullerene in 20% DMSO/chlorobenzene at ambient temperature under an oxygen atmosphere gave a penta-addition product, while the reaction of 1-alkoxy-1-siloxyalkenes or 1,2-siloxyalkenes under argon gave monoaddition products. The new method has merits over the previously reported syntheses of these compounds in that the synthesis does not require the use of heavy metals or photolysis conditions, and it can be carried out under simple and mild conditions.

- Synthesis of a Hyperbranched Polymer with Perfect Branching Based on Piperidine-4-one
  Sinananwanich, W.; Higashihara, T.; Ueda, M. *Macromolecules* **2009**, *42*, 994-1001.
  <u>Abstract:</u>



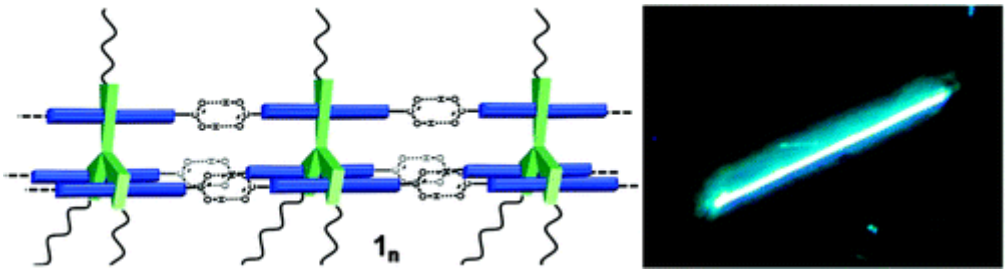
A new class of a hyperbranched polymer with 100% degree of branching has been successfully prepared by using 1-(3-phenoxypropyl)piperidine-4-one as an AB2 monomer in the presence of methanesulfonic acid. This hyperbranched polymer is based upon a piperidine-4-one ring and is designed to react with aromatic nucleophiles to give an irreversibly formed diarylated compound. The electrophilicity of piperidine-4-one is enhanced by through-space electrostatic repulsion and an inductive effect. The kinetics of the model reaction between 1-ethylpiperidine-4-one and anisole was examined. The reaction followed second-order kinetics, indicating that the first reaction, that is, the formation of the intermediate from the reaction between 1-ethylpiperidine-4-one and anisole, is considerably slower than the second one, that is, the reaction of the generated intermediate with anisole. On the basis of this observation, a new monomer, which was expected to produce a 100% branched hyperbranched polymer, was designed and synthesized. The obtained polymer was characterized by 1H and 13C NMR spectroscopy, which affirmed the 100% degree of branching of the hyperbranched polymer.

- Synthesis and Characterization of Three-Arm Poly(#-caprolactone)-Based Poly(ester#urethanes) with Shape-Memory Effect at Body Temperature.
  Xue, L.; Dai, S.; Li, Z. *Macromolecules* **2009**, *42*, 964-972.
  Abstract:



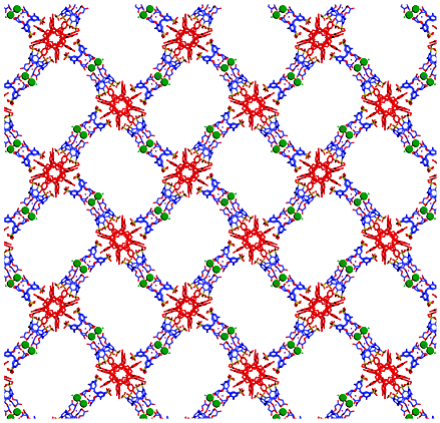
Novel biodegradable star poly(ester-urethanes) containing three-arm poly(*ε*-caprolactone) (PCL) as switching segment were prepared as shape-memory polymers (SMPs) with switching temperature (*T*s) around body temperature. PCL-triols with molecular weight (*M*n) of 2700-4200 g/mol and *T*m of 45-47 °C were synthesized in 55-67% yield by Novozym 435-catalyzed ring-opening polymerization of *ε*-caprolactone with glycerol as initiator, and their three-arm structures were confirmed by 1H and 13C NMR analysis. Reaction of the PCL-triols with methylene diphenyl 4,4′-diisocyanate isocynate and 1,6-hexanediol gave three-arm PCL-based poly(ester-urethane)s (*t*PCL-PUs) in 83-92% yield, with 65-75% soft segment. The structure of *t*PCL-Pus was confirmed by 1H NMR analysis, and the thermal properties were analyzed by DSC with *T*s of 36-39 °C. *t*PCL-PUs showed excellent shape-memory effects at 38 °C during cyclic thermomechanical tensile tests: shape recovery within 10 s, shape fixity rate of 92%, and shape recovery rate of 99%. The novel biodegradable star SMPs are potentially useful in biomedical applications.

- Highly Fluorescent Rigid Supramolecular Polymeric Nanowires Constructed Through Multiple Hydrogen Bonds
  Luo, J.; Lei, T.; Wang, L.; Ma, Y.; Cao, Y.; Wang, J.; Pei, J. *J. Am. Chem. Soc.* **2009**, *131*, 2076–2077.
  Abstract:



Supramolecular polymeric nanowires 1n constructed by a 3D shape-persistent hexaacid 1 through multiple hydrogen bonding interactions was developed. Single molecular nanoires were also obtained from its highly dilute solution.Hexaacid 1 containing π-conjugated chromophores successfully self-assembled to afford these nanofibers with high solid quantum efficiency (22%), which provides us a pathway to fabricate optoelectronic devices using these highly fluorescent nanofibers.

- Nanoporous Crystals of Calixarene/Porphyrin Supramolecular Complex Functionalized by Diffusion and Coordination of Metal Ions
  Zorzi, R. D.; Guidolin, N.; Randaccio, L.; Purrello, R.; Geremia, R. *J. Am. Chem. Soc.*, **2009**, *131*, 2487–2489.
  Abstract:

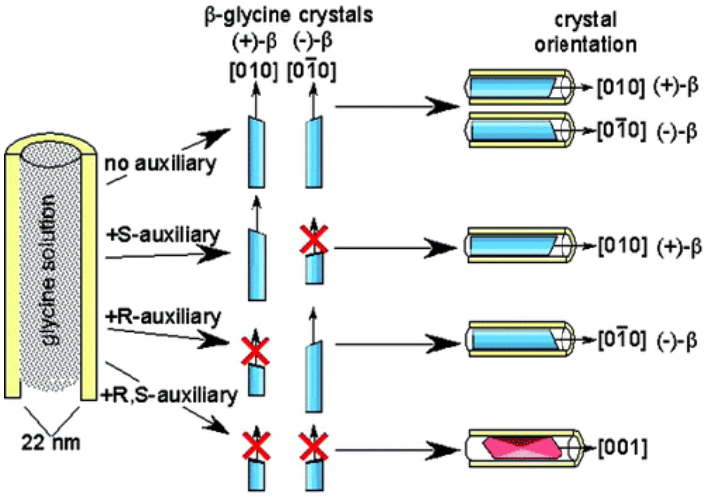


A highly nanoporous material has been obtained by self-assembly of calixarene and porphyrin building blocks. This supramolecular zeolite-like structure was successively functionalized by diffusion and coordination of metal ions to form a new bifunctionalized nanoporous material containing a porphyrinic pigment together with a metal center.

- Manipulating Crystal Orientation in Nanoscale Cylindrical Pores by Stereochemical Inhibition

Hamilton, B. D.; Weissbuch, I.; Lahav, M.; Hillmyer, M. A.; Ward, M. D. *J. Am. Chem. Soc.* **2009**, *131*, 2588–2596.

Abstract:

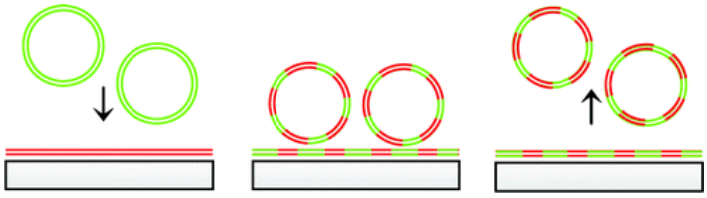


Glycine nanocrystals, grown in aligned nanometer-scale cylindrical pores of nanoporous polystyrene-poly(dimethyl acrylamide) monoliths by evaporation of imbibed aqueous solutions, adopt preferred orientations with their fast-growth axes aligned parallel with the pore direction. X-ray diffraction analysis revealed the exclusive formation of the metastable β-polymorph, with crystal size comparable with the 22 nm pore diameter, in contrast to the formation of α-glycine in the absence of nanoscale confinement. When grown from aqueous solutions alone, the nanocrystals were oriented with their [010] and [0$\bar{1}$0] axes, the native fast growth directions of the (+) and (−) enantiomorphs of β-glycine, respectively, aligned parallel with the pore direction. In contrast, crystallization in the presence of racemic mixtures of chiral auxiliaries known to inhibit growth along the [010] and [0$\bar{1}$0] directions of the enantiomorphs produced β-glycine nanocrystals with their [001] axes nearly parallel to the pore direction. Enantiopure auxiliaries that inhibit crystallization along the native fast growth direction of only one of the enantiomorphs allow the other enantiomorph to grow with the [010] axis parallel to the cylinder. Collectively, these results demonstrate that crystal growth occurs such that the fast-growing direction, which can be altered by adding chiral auxiliaries, is parallel to the pore direction. This behavior can be attributed to a competition between differently aligned crystals due to critical size effects, the minimization of the surface energy of specific crystal planes, and a more effective reduction of the excess free energy associated with supersaturated conditions when the crystal grows with its fast-growth axis unimpeded by pore walls. These observations suggest that the β-glycine nanocrystals form by homogeneous nucleation, with minimal influence of the pore walls on orientation.

- *In Situ* Preparation and Modification of Supported Lipid Layers by Lipid Transfer from Vesicles Studied by QCM-D and TOF-SIMS

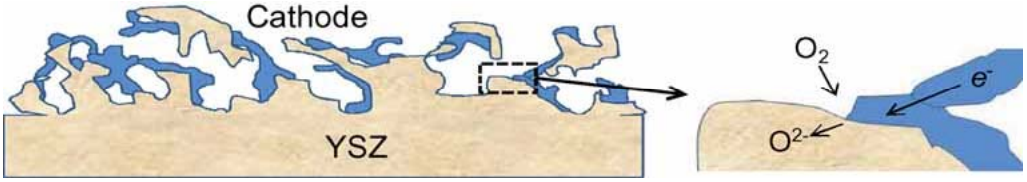
  Kunze, A.; Sj$\ddot{o}$vall, P.; Kasemo, B.; Svedhem, S. *J. Am. Chem. Soc.* **2009**, *131*, 2450–2451.

  Abstract:



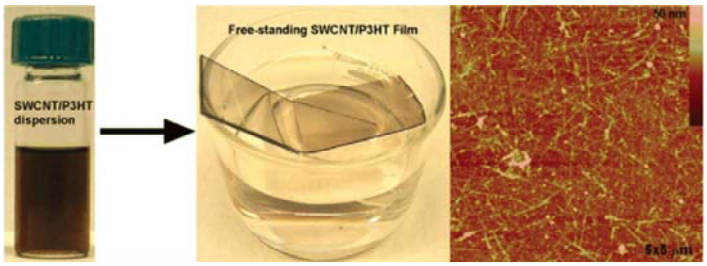
The study of lipid transfer between lipid membranes is of great interest for the fundamental understanding of this complex and important process and, furthermore, for providing a new avenue for the *in situ* modification of supported lipid bilayers (SLBs). SLBs are conveniently formed by vesicle spreading onto a solid support, but this method is limited to conditions (i.e., combination of vesicle lipid composition, surface chemical properties, and buffer) such that the vesicles break spontaneously upon adsorption to the surface. Many SLB compositions are not accessible by this approach. In the present study, we give an example of how lipid transfer can be made use of to form lipid layers with striking new features, notably with respect to stability. After lipid transfer between negatively charged POPS small unilamellar vesicles and a positively charged POEPC SLB on TiO_2, an SLB is obtained, which, upon exposure to SDS, leaves behind a lipid monolayer. It is shown how this monolayer can be used for creating new SLBs. The several step procedure, bilayer formation, lipid transfer, removal of a lipid monolayer and the reassembly of a bilayer, is monitored in real time by the quartz crystal microbalance with a dissipation (QCM-D) technique, and the lipid composition is analyzed for each step in postpreparation spectroscopic analyses using time-of-flight secondary ion mass spectrometry (TOF-SIMS). Comparison of the measured signal ratios with those of the reference samples containing known fractions of D31-POPS directly shows that the relative concentration of D31-POPS is ~50% in the SLB after D31-POPS exchange, significantly higher in the monolayer prepared *in situ* by SDS rinse, and ~20−25% after reassembly of the SLB using POEPC vesicles. The results thus provide unambiguous evidence for extensive lipid transfer between the initial POEPC SLB and D31-POPS vesicles in solution. We suggest that the reassembled SLB has a significant asymmetry between the two leaflets, and we propose that the described method is promising for the *in situ* preparation of asymmetric SLBs.

- High-Performance SOFC Cathodes Prepared by Infiltration
  Vohs, J. M.; Gorte, R. J. *Adv. Mater*. **2009**, *21*, 943-956.
  Abstract:



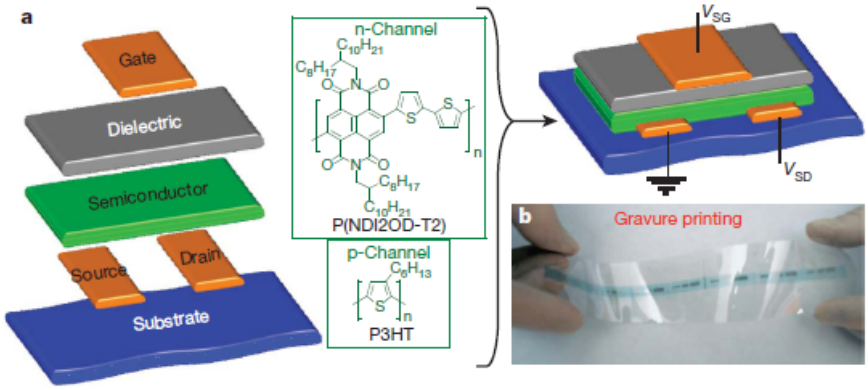
Infiltration of a porous yttria-stabilized zirconia scaffold provides for a high degree of flexibility in the choice of active materials used in the cathode of a solid oxide fuel cell. In this paper we review the infiltration method and how it is being used to produce high-performance cathodes.

- Fabrication of Free-standing, Conductive, and Transparent Carbon Nanotube Films
  Gu, H.; Swager, T. M. *Adv. Mater*. **2009**, *20*, 4433-4437.
  Abstract:



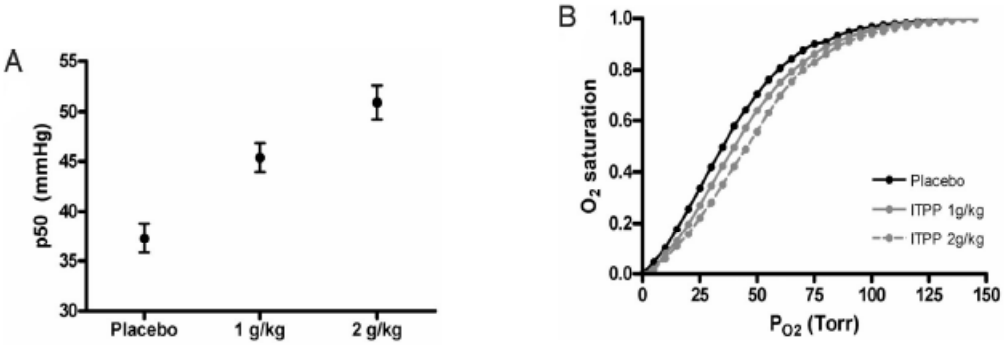
Single-walled carbon nanotube films are fabricated from a homogenous nanotube dispersion and a slow-evaporation technique. The transmittance and sheet resistance of the films are evaluated at room temperature. Using nanotube films as conductive substrates for electrochemical deposition illustrates that these nanotube films can act as alternatives to ITO for optoelectronic applications.

- A high-mobility electron-transporting polymer for printed transistors
  Yan, H.; Chen, Z.; Zheng, Y.; Newman, C.; Quinn, J. R.; Dötz, F.; Kastler, M.; Facchetti, A. *Nature* **2009**, *457,* 679-686.
  Abstract:



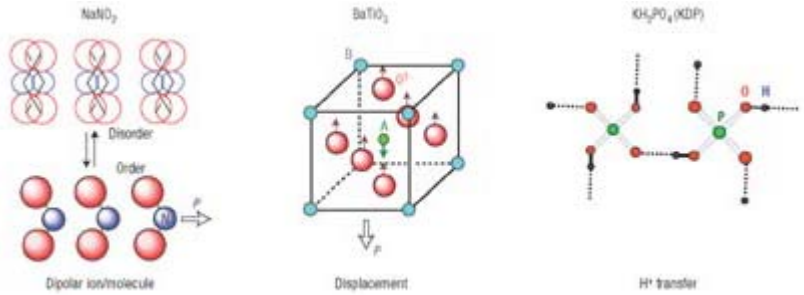
Printed electronics is a revolutionary technology aimed at unconventional electronic device manufacture on plastic foils, andwill probably rely on polymeric semiconductors for organic thin-film transistor (OTFT) fabrication. In addition to having excellent charge-transport characteristics in ambient conditions, such materials must meet other key requirements, such as chemical stability, large solubility in common solvents, and inexpensive solution and/or low-temperature processing. Furthermore, compatibility of both p-channel (hole-transporting) and n-channel (electron-transporting) semiconductors with a single combination of gate dielectric and contact materials is highly desirable to enable powerful complementary circuit technologies, where p- and n-channel OTFTs operate in concert. Polymeric complementary circuits operating in ambient conditions are currently difficult to realize: although excellent p-channel polymers are widely available, the achievement of high-performance n-channel polymers is more challenging. Here we report a highly soluble ($\sim$ 60 g l^{-1}) and printable n-channel polymer exhibiting unprecedented OTFT characteristics (electron mobilities up to $\sim$ 0.45–0.85 cm^2 V^{-1} s^{-1}) under ambient conditions in combination with Au contacts and various polymeric dielectrics. Several top-gate OTFTs on plastic substrates were fabricated with the semiconductor-dielectric layers deposited by spin-coating as well as by gravure, flexographic and inkjet printing, demonstrating great processing versatility. Finally, all-printed polymeric complementary inverters (with gain 25–65) have been demonstrated.

- Enhanced exercise capacity in mice with severe heart failure treated with an allosteric effector of hemoglobin, myo-inositol trispyrophosphate
  Biolo, A.; Greferath, R.; Siwik, D. A.; Qin, F.; Valsky, E.; Fylaktakidou, K. C.; Pothukanuri, S.; Duarte, C. D.; Schwarz, R. P.; Lehn, J.-M.; Nicolau, C.; Colucci, W. S. *Proc. Nat. Acad. Sci.* **2009**, *106*, 1342–1346.
  Abstract:



A major determinant of maximal exercise capacity is the delivery of oxygen to exercising muscles. *myo*-Inositol trispyrophosphate (ITPP) is a recently identified membrane-permeant molecule that causes allosteric regulation of Hb oxygen binding affinity. In normal mice, i.p. administration of ITPP (0.5–3 g/kg) caused a dose-related increase in the oxygen tension at which Hb is 50% saturated (p50), with a maximal increase of 31%. In parallel experiments, ITPP caused a dose-related increase in maximal exercise capacity, with a maximal increase of 57 ± 13% (P = 0.002). In transgenic mice with severe heart failure caused by cardiac-specific overexpression of Gαq, i.p. ITPP increased exercise capacity, with a maximal increase of 63 ± 7% (P = 0.005). Oral administration of ITPP in drinking water increased Hb p50 and maximal exercise capacity (+34 ± 10%; P < 0.002) in normal and failing mice. Consistent with increased tissue oxygen availability, ITPP decreased hypoxia inducible factor-1α mRNA expression in myocardium. It had no effect on myocardial contractility in isolated mouse cardiac myocytes and did not affect arterial blood pressure in vivo in mice. Thus, ITPP decreases the oxygen binding affinity of Hb, increases tissue oxygen delivery, and increases maximal exercise capacity in normal mice and mice with severe heart failure. ITPP is thus an attractive candidate for the therapy of patients with reduced exercise capacity caused by heart failure.

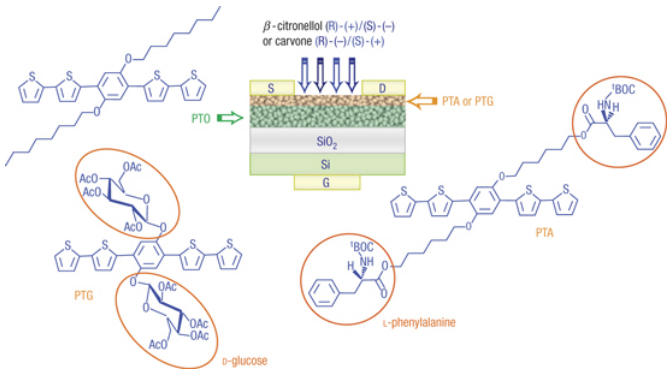
- Organic ferroelectrics
  Horiuchi, S.; Tokura, Y. *Nature Materials* **2008**, *7*, 357-366.
  Abstract:



Ferroelectricity results from one of the most representative phase transitions in solids, and is widely used for technical applications. However, observations of ferroelectricity in organic solids have until recently been limited to well-known polymer ferroelectrics and only a few low-molecular-mass compounds. Whereas the traditional use of dipolar molecules has hardly succeeded in producing ferroelectricity in general, here we review advances in the synthesis of new organic materials with promising ferroelectric properties near room temperature, using design principles in analogy to inorganic compounds. These materials are based on non-covalent molecules formed by two or more components, in which ferroelectricity arises either from molecular displacements or from the collective transfer of electrons or protons. The principle of using multi-component molecular

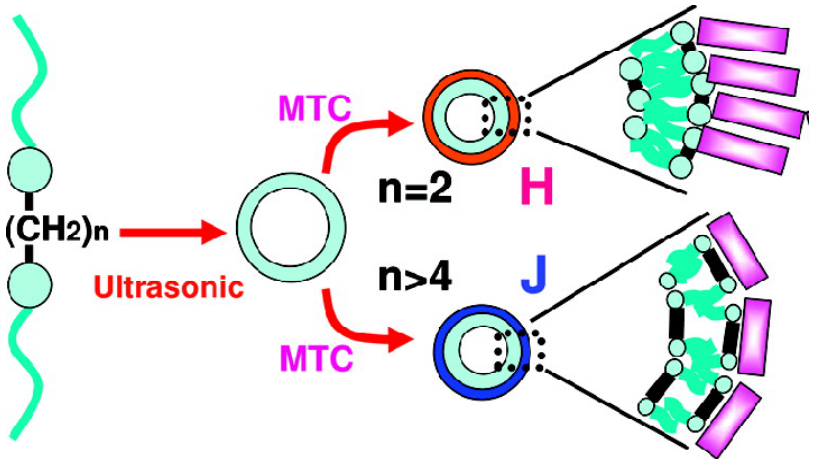
compounds leads to a much broader design flexibility and may therefore facilitate the development of future functional organics.

- A sensitivity-enhanced field-effect chiral sensor
  Torsi, L.; Farinola, G. M.; Marinelli, F. M.; Tanese, C.; Omar, O. H.; Valli, L.; Babudri, F.; Palmisano, F.; Zambonin, P. G. Naso, F. *Nature Materials* **2008**, *7*, 412-417.
  Abstract:



Organic thin-film transistor sensors have been recently attracting the attention of the plastic electronics community for their potential exploitation in novel sensing platforms. Specificity and sensitivity are however still open issues: in this respect chiral discrimination—being a scientific and technological achievement in itself—is indeed one of the most challenging sensor bench-tests. So far, conducting-polymer solid-state chiral detection has been carried out at part-per-thousand concentration levels. Here, a novel chiral bilayer organic thin-film transistor gas sensor—comprising an outermost layer with built-in enantioselective properties—is demonstrated to show field-effect amplified sensitivity that enables differential detection of optical isomers in the tens-of-parts-per-million concentration range. The ad-hoc-designed organic semiconductor endowed with chiral side groups, the bilayer structure and the thin-film transistor transducer provide a significant step forward in the development of a high-performance and versatile sensing platform compatible with flexible organic electronic technologies.

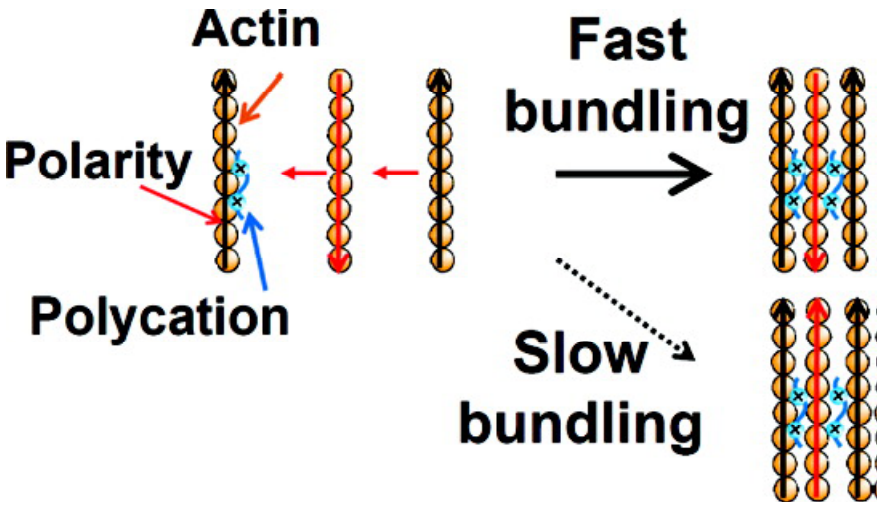
- Spacer-Modulated Aggregation of the Cyanine Dye on the Vesicles of Gemini Amphiphiles
  Zhang, G.; Zhai, X.; Liu, M.; Tang, Y.; Huang, X.; Wang, Y. *Langmuir* **2009**, *25*, 1366-1370.
  Abstract:



A series of gemini amphiphiles (bis(2□-heptadecyl-3□-ethylimidazolium)-1,*n*-alkane dibromide, abbreviated as Gn, *n*) 2, 4, 6, 8, 10) was found to form vesicles under ultrasonication in aqueous

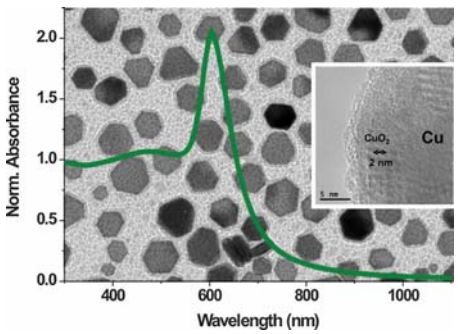
solution at very low concentration (5 μM), which was confirmed by dynamic light scattering (DLS) and transmission electron microscopy (TEM). The adsorption and interaction of a cyanine dye (3,3′-disulfopropyl-4,5,4′,5′-dibenzo-9-methyl-thiacarbocyanine triethylammonium salt, abbreviated as MTC) on the vesicles was investigated. It was found that the cyanine dye could exhibit different colors when interacting with the vesicles. The UV-vis spectral measurements revealed the formation of the H or J aggregates of the cyanine dye on the vesicles, which is spacer length dependent: the short spacer length prefers the formation of the H-aggregate, whereas the longer spacer favors the J-aggregate formation. In addition, these aggregates showed different absorption positions from those on the planar films. Furthermore, by mixing the G2 and G10 vesicles in different ways, the selective aggregation of the cyanine dye on the vesicles was realized.

- Mechanism on Polarity Sorting of Actin Bundles Formed with Polycations
  Shikinaka, K.; Kakugo, A.; Osada, Y.; Gong, J. P. *Langmuir*, **2009**, *25*, 1554-1557.
  Abstract:



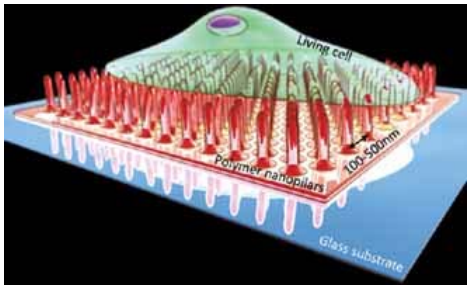
In this paper we explored factors that determine the polarity of an Actin bundle formed with polycation through electrostatic interaction. We found that the polarity decreases with an increase in the polycation concentration while it hardly depends on the KCl salt concentration. Additionally, the polarity of the Actin bundle increases with an increase in the degree of polymerization of the polycation at a constant polymer concentration. From these results we proposed that the kinetics of nuclei formation determines the polarity of the Actin bundle.

- Aerobic Synthesis of Cu Nanoplates with Intense Plasmon Resonances
  Pastoriza-Santos , I.; Sánchez-Iglesias, A.; Rodríguez-González, B.; Liz-Marzán, L. M. *Small* **2009**, *5*, 440-443.
  Abstract:



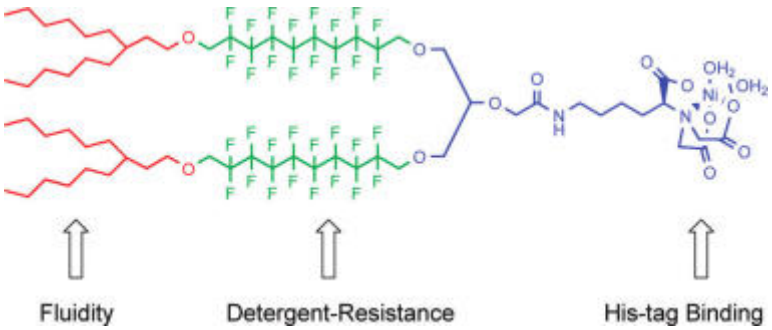
Single-crystalline Cu nanoplates with a prominent in-plane dipole surface plasmon band are fabricated through reduction of copper salt with hydrazine using PVP as stabilizer and no need for inert atmosphere. Due to the lower free-electron character of copper, the interband transitions overlap, and therefore damp, the out-of-plane dipole plasmon resonance

- Large-Scale Ordered Plastic Nanopillars for Quantitative Live-Cell Imaging
  Sengupta, K.; Moyen, E.; Macé, M.; Benoliel, A.-M.; Pierres, A.; Thibaudau, F.; Masson, L.; Limozin, L.; Bongrand, P.; Hanbücken, M. *Small* **2009**, *5*, 449-453.
  Abstract:



Transparent nanopatterned plastic substrates are prepared by molding a photopolymer inside nanoporous ordered anodic alumina and subsequently etching away the mold. The array of glass-supported, index-matched nanopillars is ordered over a large area. They can serve as a platform for studying the interaction of living cells with nanotopography (see image) using quantitative optical microscopy.

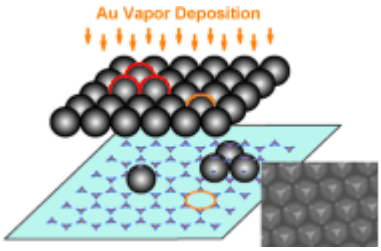
- Synthesis of Nickel-Chelating Fluorinated Lipids for Protein Monolayer Crystallizations
  Hussein, W.; Ross, B.; Landsberg, M.; Lévy, D.; Hankamer B.; and McGeary, R. *J. Org. Chem.* **2009**, *74*, 1473–1479.
  Abstract:



Nickel-chelating lipids have been synthesized for use as functionalized templates for 2-D crystallization of membrane proteins. These monolayer-forming lipids have been designed with three distinct components: (i) a branched hydrocarbon tail to confer fluidity of the monolayer, (ii) a perfluorinated central core for detergent resistance, and (iii) a nickel-chelating hydrophilic headgroup to facilitate binding of recombinant, polyhistidine-tagged fusion proteins. Alkylations of fluorinated alcohols used in these syntheses proceed in good yields only with the application of prolonged sonication and, in some cases, in the presence of phase-transfer catalysts. Formation of 2-D crystals of the His-tagged membrane protein BmrA from *Bacillus subtillis* is reported.

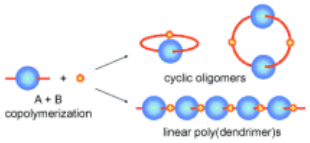
- Colloidal Lithography—The Art of Nanochemical Patterning
  Zhang, G.; Wang, D. *Chem. Asian J.* **2009**, 4, 236 – 245.

Abstract:



Colloidal lithography relies on using colloidal crystals as masks for etching and deposition, and allows fabrication of various nanostructures on planar and non-planar substrates with low-cost, high-throughput-processing, large fabrication area, and a broad choice of materials. The feature size can easily shrink by decreasing the microsphere diameter in the colloidal mask. The feature shape can be diversified by varying the crystal structure of the colloidal mask, etching the mask, altering the incidence angle of the vapor beam, and stepwise manipulation of the mask registry. This nanochemical patterning strategy paves a complementary way to conventional top-down lithography. This focus review provides an overview of the principle of colloidal lithography, and surveys the recent developments as well as outlining the future challenges.

- Synthesis of Organometallic Poly(dendrimer)s by Macromonomer Polymerization: Effect of Dendrimer Size and Structural Rigidity on the Polymerization Efficiency
  Cheung, S.-Y.; Chow, H.-F.; Ngai, T.; Wei, X. *Chem. Eur. J.* **2009**, *15*, 2278-2288.
  Abstract:

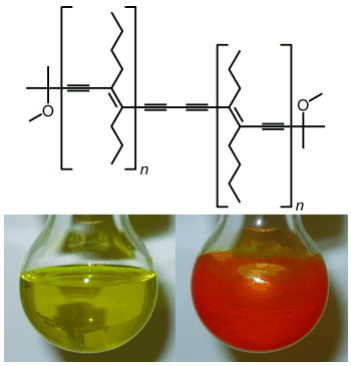


Cyclization versus propagation: The copolymerization behavior of a dendritic macromonomer with a metal-containing linker is controlled by the dendrimer size and its structural rigidity. Structurally more flexible dendritic monomers tend to form more cyclic oligomers than structurally rigid monomers (see figure).
Two series of first to third generation (G1-G3) oligoether dendrimers, one bearing a shorter spacer chain (C—O) and the other having a longer spacer branch (C—C—C—O) were prepared. Both series of compounds, containing two reactive C≡CH moieties on the dendrimer surface, were used as macromonomers and copolymerized with *trans*-[$Pt(PEt_3)_2Cl_2$] to form organometallic poly(dendrimer)s by an outer-sphere-outer-sphere connection strategy. It was found that concentration of monomer used in the polymerization, the dendrimer generation, and, most strikingly, the length of the spacer were key factors that determined the polymerization efficiency. Hence, the structurally more rigid and compact C—O linked dendrimers formed poly(dendrimer)s with a higher degree of polymerization than the structurally less rigid and more bulky C—C—C—O dendrimers. This result was due to the higher tendency to form cyclic oligomers in the latter series of compounds. In addition, the differences in the polymerization efficiency among the three generations of dendrimers could be explained by the gradual decrease of reactive functional group density on the dendrimer surface.

- Synthesis and Optoelectronic Properties of Nanometer-Sized and Highly Soluble Homocoupled Oligodiacetylenes

Pilzak, G. S.; Baggerman, J.; van Lagen, B.; Posthumus, M. A.; Sudhölter, E. J. R.; Zuilhof, H. *Chem. Eur. J.* **2009**, *15*, 2296-2304.

Abstract:



Color and shape of oligodiacetylenes: We synthesized a series of highly soluble homocoupled oligodiacetylenes (HODAs). The color of these oligomers is dependent on the molecular length and aggregation state (see picture). The optical properties of these materials were studied by using both steady-state and time-resolved spectroscopic techniques.

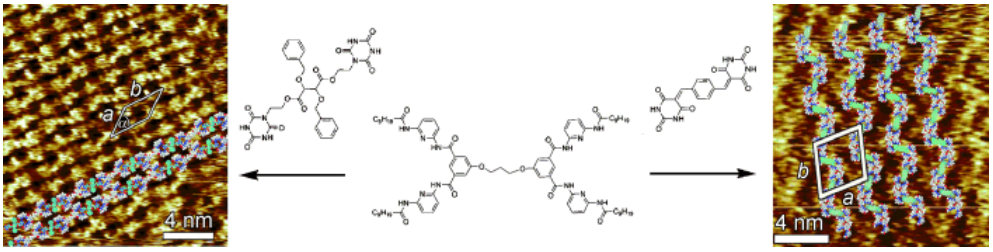
A new series of pure, nanometer-sized and highly-soluble homocoupled oligodiacetylenes (HODA) consisting of two symmetrical oligodiacetylene units was synthesized with high yield and on a multi-milligram scale under mild, catalytic Sonogashira conditions. The λ_{max} and the ε_{max} of absorption for these HODAs show an increase with the chain elongation. The λ_{max} converges to 450 nm for the longest members of the series at micromolar concentration and to 462 nm for thin drop-casted films. An additional red-shifted absorption is observed in the solid state and in solution at low temperatures, which is caused by aggregation. The λ_{max} of the fluorescence emission increases with the chain length and reaches 492 nm for the longest oligomer. The fluorescence quantum yield has its maximum for the shortest oligomer and decreases rapidly for the longer ones. A similar trend is found for the fluorescence lifetime with a maximum of 100 ps for the homocoupled monomer. The rotational correlation time shows a linear increase with the oligomer length. This reveals a significant persistence length and indicates that the HODA molecules are fully stretched molecular rods (up to 8.2 nm).

- Tuning the Supramolecular Chirality of Polyaniline by Methyl Substitution
  Yan, Y.; Deng, K.; Yu, Z.; Wie, Z. *Angew. Chem. Int. Ed.* **2009**, *48*, 2003 –2006.
  Abstract:

A game of Twister: The induced helicity of polyaniline and its supramolecular structures could be tuned by the methyl substitution of one of the monomers. By copolymerization of aniline with *m*-toluidine, the helicity of copolymer (PMANI) nanofibers was totally inverted compared to that of

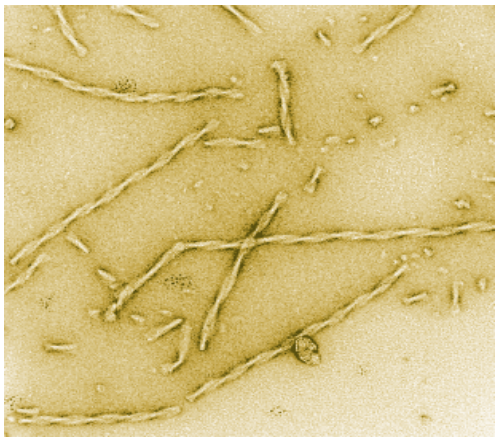
polyaniline (PANI), while copolymer nanofibers with *o*-toluidine (POANI) had the same helicity as that of polyaniline (see picture).

- STM Insight into Hydrogen-Bonded Bicomponent 1 D Supramolecular Polymers with Controlled Geometries at the Liquid-Solid Interface
  Ciesielski, A.; Schaeffer, G.; Petitjean, A.; Lehn, J.-M.; Samori, P. *Angew. Chem. Int. Ed.* **2009**, *48*, 2039 –2043.
  Abstract:



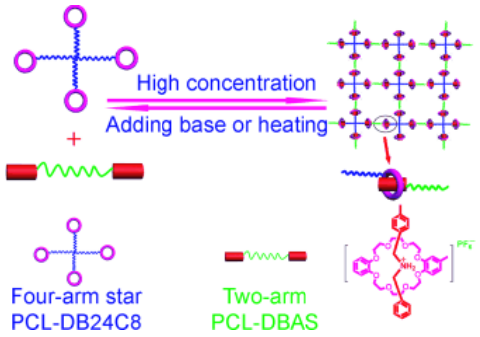
Bicomponent supramolecular polymers, consisting of two alternating molecules bridged through six H-bonds, are observed by STM at the solid-liquid interface. Control of the geometry of the 1D architecture was obtained by using two different connecting molecules with different conformational rigidity, affording either linear (see picture, left) or zigzag (right) motifs.

- Development of Tau Aggregation Inhibitors for Alzheimer's Disease
  Bulic, B.; Pickhardt, M.; Schmidt, B.; Mandelkow, E.-M.; Waldmann, H.; Mandelkow, E.
  Angew. Chem. Int. Ed. **2009**, *48*, 1740 – 1752.
  Abstract:



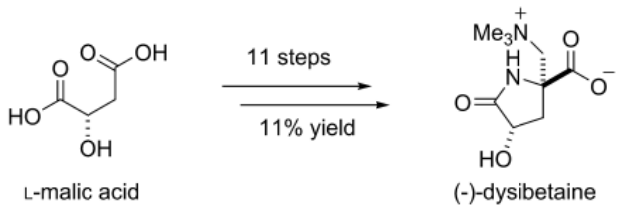
Small molecules against Alzheimer's: The pathological aggregation of the tau protein is a major hallmark of neurodegenerative diseases such as Alzheimer's disease. The inhibition or reversal of tau aggregation is a potential therapeutic strategy that is currently undergoing clinical trials. The image shows pathological fibers assembled from tau protein, which are the main components of the neurofibrillary tangles of Alzheimer's disease.

- Responsive Supramolecular Gels Constructed by Crown Ether Based Molecular Recognition
  Ge, Z.; Hu, J.; Huang, F.; Liu, S. *Angew. Chem. Int. Ed.* **2009**, *48*, 1798 –1802.
  Abstract:



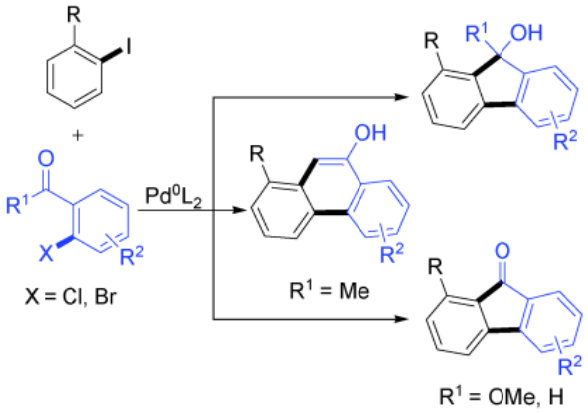
Responsive supramolecular gels were constructed from crown ether terminated four-arm star poly(ε-caprolactone) (PCL-DB24C8) and dibenzylammonium-terminated two-arm PCL-DBAS (see scheme), exploiting the formation of pseudorotaxane linkages between crown ether and ammonium moieties. The resultant supramolecular gels exhibit thermo- and pH-induced reversible gel-sol transition

- An Ugi Reaction in the Total Synthesis of (-)-Dysibetaine
  Isaacson, J.; Kobayashi, Y. *Angew. Chem. Int. Ed.* **2009**, *48*, 1845 –1848.
  Abstract:



(-)-Dysibetaine has been synthesized in 11 steps from readily available L-malic acid (see scheme). The key step is a unique Ugi 4-center-3-component cyclization reaction, where an ester group acts as the carboxylic acid component. The use of 1,1,1,3,3,3-hexamethyldisilazane as an ammonia equivalent and a specially designed isocyanide leads to an expeditious synthesis.

- Exploiting the Divergent Reactivity of Aryl-Palladium Intermediates for the Rapid Assembly of Fluorene and Phenanthrene Derivatives
  Zhao, Y.-B.; Mariampillai, B.; Candito, D. A.; Laleu, B.; Li, M.; Lautens, M. *Angew. Chem. Int. Ed.* **2009**, *48*, 1849 –1852.
  Abstract:



They all fall down: The value of domino processes can be greatly enhanced when the possibility exists for one to selectively diverge from a common intermediate. In preliminary studies the dual reactivity of aryl-palladium intermediates is exploited. A diverse array of fluorene and phenanthrene derivatives were synthesized in a rapid and efficient manner (see scheme).